Quantitative speciation of aerosols through in-situ GC×GC in Pasadena, CA during the CalNex 2010 experiment

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Overview

• GC×GC Thermal Desorption Gas Chromatograph/Mass Spectrometer (2D-TAG) deployed in Pasadena, CA as part of the California at the Nexus between Air Quality and Climate Change (CalNex) Experiment in the summer of 2010 (for details and overview of TAG system see Williams et al., 2006)

• Over 100 compounds quantified, several hundred more observed
  • Includes alkanes, alkenes, furanones, ketones, nitriles, phthalic acids, polycyclic aromatic hydrocarbons (PAHs), branched PAHs, and oxygenated PAHs
  • Many known tracers for secondary as well as primary organic aerosol

• High time resolution allows analysis of the variability and covariance of compounds, used to better understand sources

• Gas-particle partitioning measured by alternating filtered/unfiltered samples

Methodology

Sample is collected and analyzed using a GC×GC Thermal Desorption Gas Chromatograph (2D-TAG) coupled to a Time-of-Flight Mass Spectrometer:

• Ambient air passed through a 2.5 um cyclone

• Filter switched in and out of path – **allows gas-particle partitioning measurements**

• Particles impacted into custom collection and thermal desorption (CTD) cell

• Desorbed from CTD cell and injected into gas chromatograph through custom valveless injection box

• Separated using GC×GC: first dimension column separates based on volatility, second dimension column separates based on polarity

  • Custom interface modulator recondenses eluent then introduces it onto second column at 5 second intervals using forced air cooling followed by resistive heating (for details see Worton et al., *in review*)

• Quantified using regularly injected deuterated internal standard, eliminating error from run-to-run variability

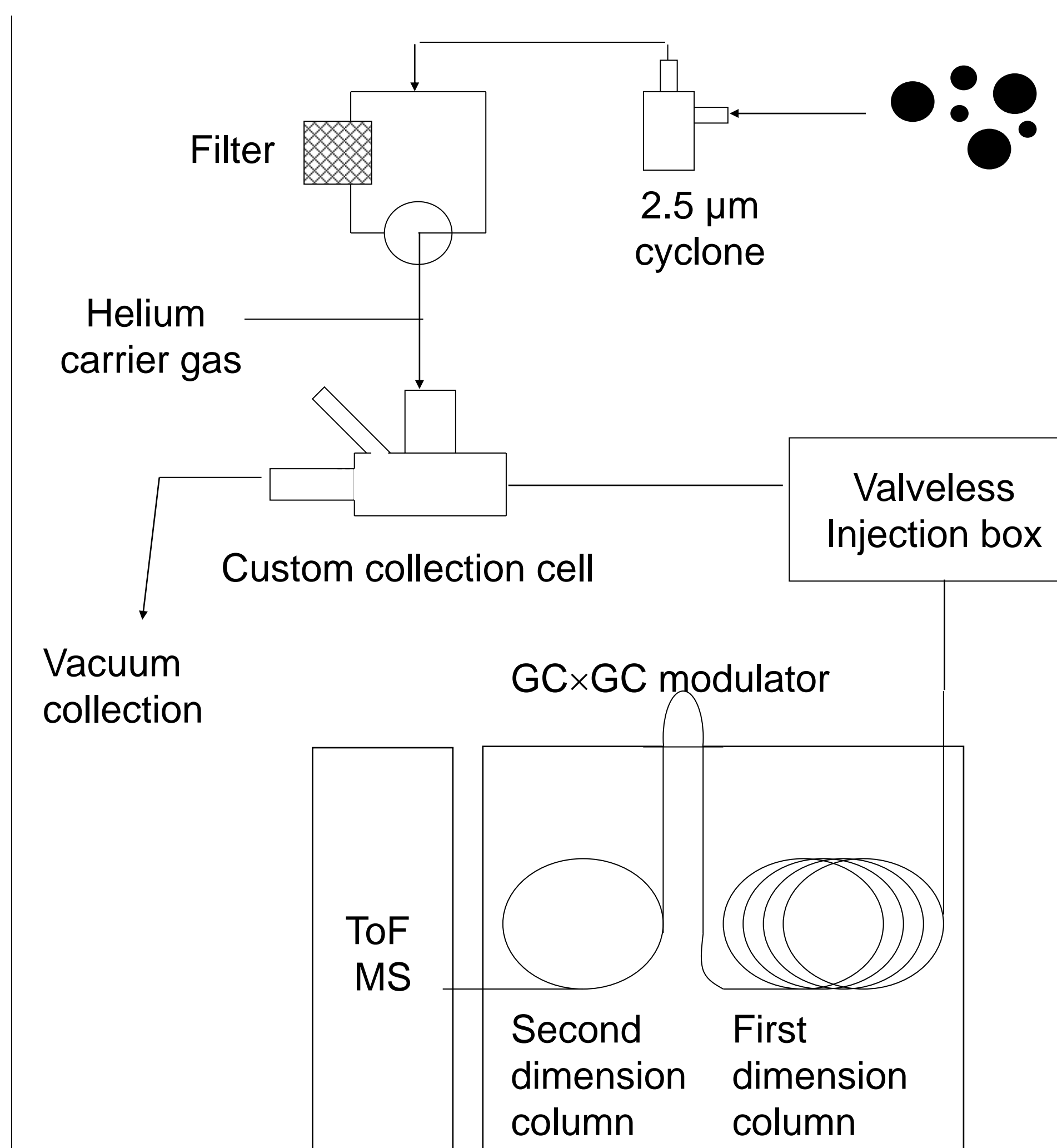**Samples collected with 2-hour time resolution**

Figure 1. Schematic of 2D-TAG configuration
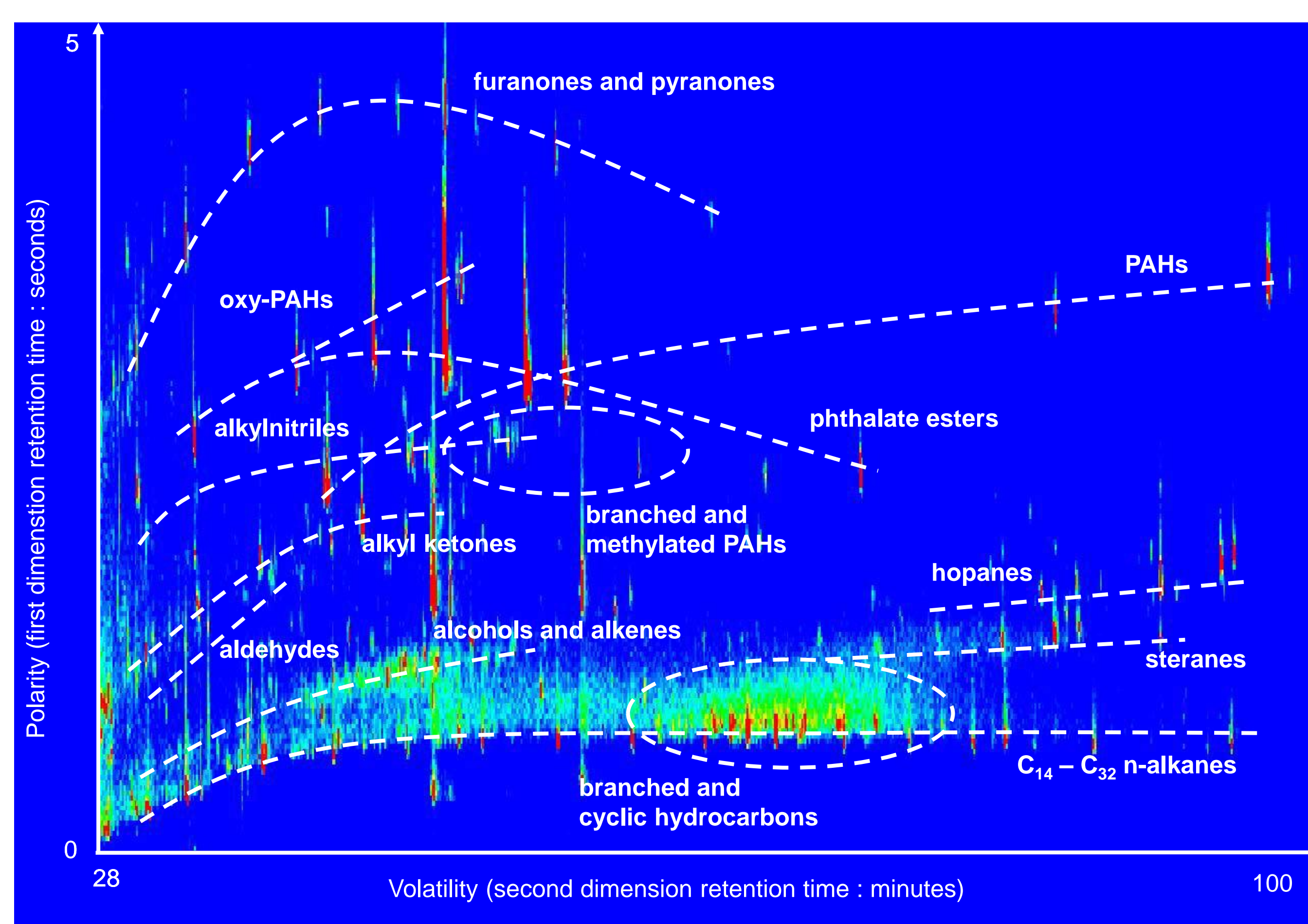
Results

Figure 2. Typical GC×GC chromatogram from this data (collected June 14th, 2010)

Families of compounds are separated in two dimensions, improving identification and separation of many trace compounds

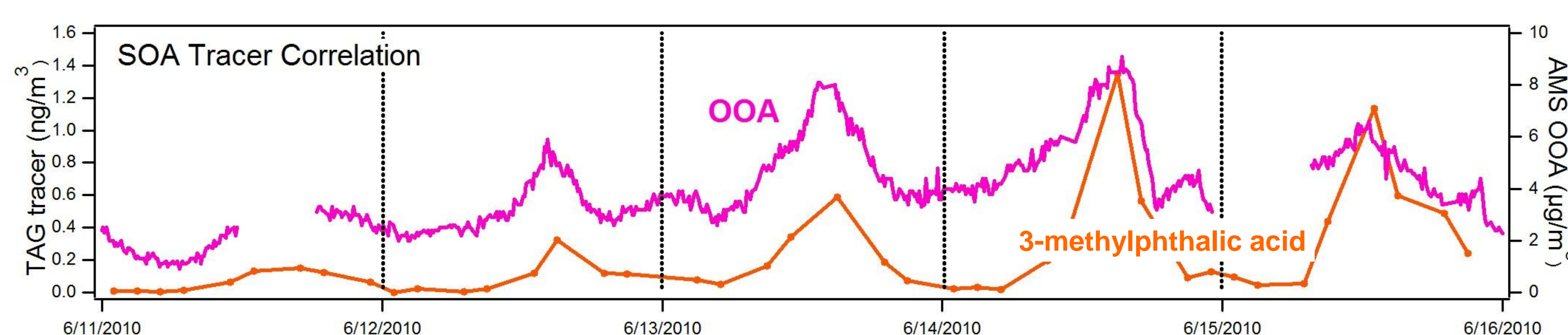### Covariance and Source Profiles

Figure 3. Time series of known particle-phase tracer for secondary organic aerosol. Tracer compounds correlate well with oxygenated and hydrocarbon-like organic aerosol (HOA and OOA) from the Aerodyne Aerosol Mass Spectrometer (AMS)

Quantified particle-phase tracers include: **methylphthalic acid** (SOA), **naphthalic acid** (SOA), **fluorenone** (SOA?), **pentadecanone** (SOA?), **hopanes** (POA), PAHs such as **chrysene** (POA), **octadecanenitrile** (meat-cooking), and **retene** (biomass burning)

Partitioning

$$\text{Particle fraction} = \frac{\text{signal from unfiltered run} - \text{signal from filtered run}}{\text{signal from unfiltered run}}$$

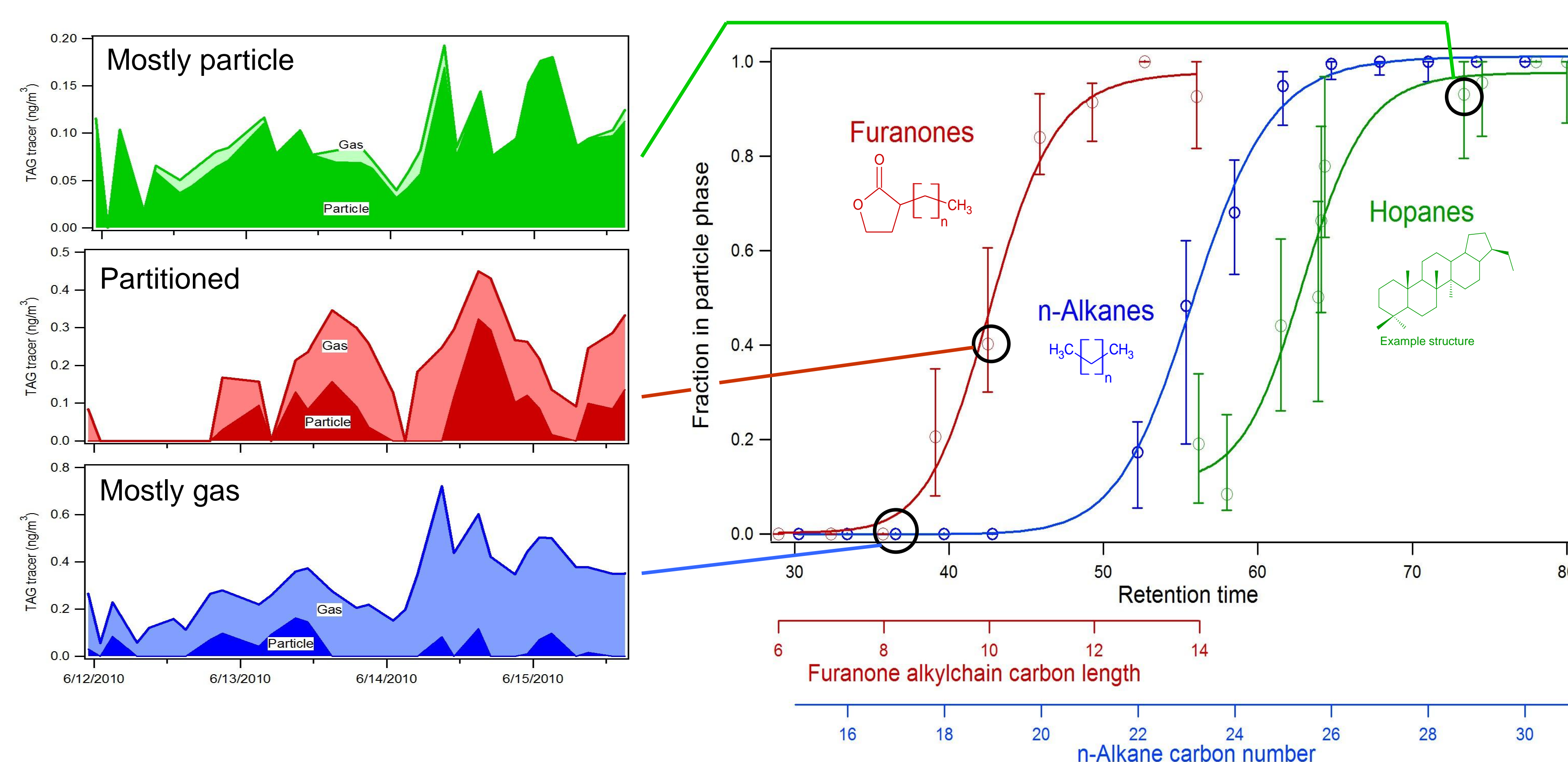**Allows *in-situ* measurement of gas-particle partitioning**

Figure 4. *In-situ* partitioning measurements for three compound families. Three example compounds (left) illustrate typical partitioning time series. Median fraction in the particle phase (right; error bars represent quartiles) qualitatively match those expected from theory. Some over prediction of particle phase is expected due to partial collection of semi-volatiles

Conclusions

• High time resolution multi-dimensional chromatography allows better identification and separation of aerosol constituents

• Correlations between constituents form complex source profiles to be used for source apportionment

• Real time gas-particle partitioning estimated by the filter difference method yields results similar to those expected from partitioning theory (Odum et al, 1996)

• Regular injection of a deuterated internal standard allows improved calibration and quantitation of tracer compounds

References
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• Williams, B. J., Goldstein, A. H., Kreisberg, N. M., and Hering, S. V.: An In-Situ Instrument for Speciated Organic Composition of Atmospheric Aerosols: Thermal Desorption Aerosol GC/MS-FID (TAG), Aerosol Sci. Tech., 40, 627-638, 2006.